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The ^2D Rydberg series in Al I

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Abstract

High-quality *ab initio* electronic structure calculations have been performed on the ^2D Rydberg series in Al I. The configuration $3s3p^2(^2D)$ is shown to contribute substantially to the lowest four ^2D Rydberg states. The same configuration also contributes substantially to a ^2D state embedded in the ionization continuum. Corrected oscillator strengths for the first six members of the ^2D Rydberg transitions are given: these should be of substantially higher accuracy than currently available values.

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Some controversy exists concerning the assignment of the $3s^2nd(^2D)$ Rydberg series in Al I. It was pointed out some time ago (see, for example, Moore (1949) and refs. therein) that one of the lowest terms in the ^2D sequence might correspond to the configuration $3s3p^2$, and that the assigned term numbering might therefore have to be revised. Based on an analysis of the intensity of the lowest $^2P - {}^2D$ transition, Budick (1966) concluded that the lowest ^2D state should indeed be identified with the configuration $3s3p^2$. However, experimental results reported by Garton (1962) (see also Eriksson and Isberg (1963)) support the assignment of all observed terms in the series as $3s^2nd$. This latter identification is the generally accepted one, as it is also consistent with theoretical studies by Weiss (1973). Although those theoretical studies clearly demonstrate considerable configuration mixing between the $3s3p^2$ and $3s^23d$ terms, there have been no investigations considering possible mixing between $3s3p^2$ and higher nd terms. It is therefore still unclear whether the $3s3p^2$ configuration is simply distributed among the various terms of the ^2D Rydberg series or whether there is some other state that is substantially derived from $3s3p^2$. Experimental observations by Garton (1962) suggest that a state lying beyond the ionization limit of the ^2D series is derived principally from the $3s3p^2$ configuration.

In the present work, we report the results of very accurate *ab initio* calculations on the ^2D series in Al I. The configuration $3s3p^2(^2D)$ is found to contribute substantially (more than 50%) to the lowest four members of the series; the remainder of the configuration lies some 1000 cm^{-1} beyond the ionization limit. In addition, we have computed oscillator strengths for a number of terms in the series. The results are expected to be much more accurate than the rather discordant values presently available in compilations. The oscillator strengths for the lowest states show substantial perturbation by the $3s3p^2$ configuration, but the configuration mixing causes little deviation from the Rydberg formula for the excitation energies.

The results reported here are obtained with full CI calculations in which only the three Al valence electrons are correlated. The $1s$, $2s$ and $2p$ core orbitals are held fully occupied in the form obtained from an atomic SCF calculation on Al $3s^23p(^2P)$, and the full CI configuration space results from allocating the three valence electrons in all possible ways (consistent with the desired spin and spatial

symmetry) among the remaining orbitals. The orbitals are expanded in a basis set of contracted Gaussian functions: this basis is derived from a $(20s\ 13p)$ primitive set, obtained using the even-tempered parameters of Schmidt and Ruedenberg (1979), augmented initially with a $(6d\ 4f)$ polarization set and then with additional diffuse d sets, as discussed below. The initial $6d$ set is an even-tempered sequence of the form $\alpha\beta^k, 0 \leq k \leq 5$ with $\alpha = 0.03$ and $\beta = 2.5$. The $4f$ set is an even-tempered sequence with $\alpha = 0.10$ and $\beta = 2.5$. This $(20s\ 13p\ 6d\ 4f)$ primitive set is contracted using atomic natural orbitals (ANOs) (Almlöf and Taylor 1987) from a sir reference single and double excitation CI calculation on the Al ground state. The contracted functions comprise the first five s, four p, two d and two f ANOs, plus the outermost two s, two p, two d and f primitives, which are left uncontracted to improve the flexibility of the description of the outer regions of the charge density. The resulting basis can be denoted $[7s\ 6p\ 4d\ 3f]$. Various sets of additional diffuse d functions are added to the basis to describe the d Rydberg states: these sets comprise an even-tempered sequence added to the above d set, with $\beta = 2.5$. These added sets are denoted $+(3d)$, $+(5d)$ and $+(7d)$.

The full CI calculations are performed in an orbital basis defined by SCF calculations on the Al and Al^+ ground states. Full atomic symmetry and equivalence restrictions are imposed. SCF orbitals for Al $3s^23p(^2P)$ are used for the s, p and f symmetries, while the orbitals for the d symmetry are obtained from an SCF calculation on Al^+ $3s^2(^1S)$. The full CI energies and total wave functions are, of course, invariant to any unitary transformation on the orbitals included in the full CI wave function: the advantage of using d orbitals from the positive ion is that each ^2D Rydberg state is dominated by a single d orbital in the configuration $3s^2nd$. This makes it easier to analyze the wave functions of the various terms.

The ^2D excitation energies, relative to ground-state Al, are given in Table 1 for various diffuse d sets. Also included are the computed ionization limit, the $3s3p^2(^2P)$ excited state excitation energies, the corresponding experimental results (Moore 1949) and the fraction of each ^2D Rydberg state derived from the term $3s3p^2(^2D)$. The lowest ^2D state excitation energies are relatively unaffected by extension of the d space beyond the addition of the $(3d)$ diffuse set, while each additional d function added allows one more Rydberg state to be properly described.

The agreement between the computed and experimental results is excellent: the lowest excitation energy is underestimated by less than 250 cm^{-1}, while the excitation energy for the highest state considered ($3s^2 10d$) is overestimated by only a little over 300 cm^{-1}. The most likely source for these discrepancies, at least for the lower members of the series, is the omission of core-valence correlation effects. The computed ionization potential is only 100 cm^{-1} less than the experimental value, while the error in the $3s3p^2(^2P)$ excitation energy is slightly larger than for the $3s^2nd$ series. This again is likely to be due to the differential effects of core-valence correlation.

It can be seen from Table 1 that the configuration $3s3p^2(^2D)$ makes a substantial contribution to the lowest few ^2D states. This contribution is obtained as the square of the coefficient of this configuration in the various normalized full CI wave functions, expressed as a percentage. The computed contributions converge well with the expansion of the d basis, as do the excitation energies. The $3s3p^2(^2D)$ term contributes essentially nothing to the $n = 8$ and higher Rydberg states. The contribution to the lowest Rydberg state is similar to the value of 21% obtained by Weiss (1973), although no excitation energy is given in his review. Matos *et al.* (1987) obtain a larger percentage, but, as these authors point out, their d basis (which was developed for AlH) is not sufficiently diffuse to describe the $3s^2 3d$ term accurately.

As Weiss (1973) hypothesized, a major part of the $3s3p^2(^2D)$ configuration is thus "smeared out" over the ^2D Rydberg series, although the larger number of Rydberg states computed in the present work indicates that this smearing is confined to the lowest few states. However, the present work also shows an additional ^2D state, labelled A in Table 1, at about 1000 cm^{-1} beyond the ionization limit, which has a substantial contribution from $3s3p^2$. This seems to agree very well with the assertion of Garton (1962) that a diffuse doublet, which occurs "a short way beyond" the ionization limit, is in fact the $3s3p^2(^2D)$ term. (Unfortunately, Garton's review contains no quantitative information on the location of this doublet.) Such a state is expected to be diffuse, as it will couple to ionizing states in the continuum of Al II $3s^2$, but as the $3s3p^2$ term itself cannot autoionize to this limit in a one-electron process, the observed doublet will show a band-like, rather

than continuum-like, structure.

We also list in Table 1 oscillator strengths for a number of transitions of the form $^2P \rightarrow {}^2D$. Transition moments are computed in the dipole length formulation. Apart from the perturbation in the lowest few values caused by the $3s3p^2$ configuration, the results follow the expected trend. The term arising from the remainder of the $3s3p^2$ configuration carries considerable intensity, as expected for a dipole transition with no change in principal quantum number. Of course, a full treatment of the intensity of transitions to this state would involve coupling to the continuum, which is beyond the scope of this work. It is interesting that the perturbing effects of the $3s3p^2$ configuration are confined to intensities — the excitation energies for the entire Rydberg series fit extremely well (both for the computed and experimental values) to the conventional empirical Rydberg formula. The oscillator strength for the lowest transition is in excellent agreement with the level-crossing spectroscopy result of Budick (1966). However, his contention that this supports a $3s3p^2$ configuration for the lowest ^2D state must be rejected: inadequacies in the Coulomb model used in analyzing the lifetimes are probably responsible for the error. Given that core relaxation and correlation effects do not affect the lifetimes (which is supported by other calculations on Al (Weiss 1973)) wave functions of the quality used in this work would be expected to yield lifetimes accurate to better than 10%, consistent with the agreement between this work and Budick's measurements. However, while the overall trend in our computed oscillator strengths across the series agrees qualitatively with that of the experimental results given by Penkin and Shabanova (1963,1965), the values themselves agree very poorly. Penkin and Shabanova overestimate considerably the oscillator strength for the lowest transition, so in the tables of Wiese *et al.* (1969) their results have been rescaled to agree with Budick's value for the lowest transition. Even with such rescaling the results do not agree with our computed values to within Wiese's suggested error bars of $\pm 25\%$. It seems very unlikely that our results would show random deviations from the true values, and no systematic error (which in view of the quality of the results is unlikely anyway) in the computed results can explain the discrepancy. It seems probable that the Penkin and Shabanova results are not as reliable as the uncertainty estimate of Wiese *et al.* suggests.

The $3s3p^2(^2D)$ term has been shown to contribute significantly to the lowest few ^2D Rydberg states of Al I; the residuum from these contributions appears about 1000 cm^{-1} beyond the ionization limit that gives ground-state Al II. The oscillator strengths for the lowest few transitions in the ^2D series are strongly perturbed by the $3s3p^2$ configuration, in general agreement with the available experimental results, but quantitative agreement between the computed and experimental oscillator strengths is obtained only for Budick's measurement of the lowest transition. In view of the quality of the present calculations we suggest that the oscillator strengths of Penkin and Shabanova are not reliable.

References

Almlöf J and Taylor P R 1987 J. Chem. Phys. **86** 4070

Budick B 1966 Bull. Am. Phys. Soc. **11** 456

Eriksson K B S and Isberg I B S 1963 Arkiv Fysik **23** 527

Garton W R S 1962 in "Proceedings of the Fifth Conference on Ionization Phenomena in Gases, 1961" (Amsterdam: North-Holland)

Matos J M O, Malmqvist P-Å and Roos B 1987 J. Chem. Phys. **86** 5032

Moore C E 1949 "Atomic Energy Levels, Vol I" (Washington: National Bureau of Standards)

Penkin N P and Shabanova L N 1963 Opt. Spectry. **14** 5

Penkin N P and Shabanova L N 1965 Opt. Spectry. **18** 504

Schmidt M W and Ruedenberg K 1979 J. Chem. Phys. **71** 3951

Weiss A W 1973 Adv. At. Mol. Phys. **9** 1

Wiese W L, Smith M W and Miles B M 1969 "Atomic Transition Probabilities, Vol II" (Washington: National Bureau of Standards)

Table 1. Full CI excitation energies[a] (cm^{-1}) and oscillator strengths for states of Al I.

	ΔE				$3s3p^2(^2D)$[b]			$f_{ik}(^2P \rightarrow {}^2D)$	
Configuration	+(3*d*)[c]	+(5*d*)	+(7*d*)	Expt[d]	+(3*d*)	+(5*d*)	+(7*d*)	+(5*d*)	Expt[e]
$3s^23d$	32189	32189	32189	32436	23.9	23.9	23.9	0.166	0.230(0.175)
$3s^24d$	38664	38664	38664	38931	22.7	22.7	22.7	0.077	0.057
$3s^25d$	42083	42142	42079	42236	12.6	12.5	12.5	0.150	0.157
$3s^26d$	44099	44063	44071	44168	7.2	6.1	6.1	0.110	0.127
$3s^27d$		45262	45262	45345		2.5	2.5	0.055	0.085
$3s^28d$		46131	46110	46094		1.7	1.9	0.014	0.056
$3s^29d$			46785	46594			< 1		
$3s^210d$			47290	46942			< 1		
I.P.			48179	48279					
A $3s3p^2(^2D)$[f]	48840	49189	49225		19.1	17.4	17.2	1.270	
$3s3p^2(^2P)$	56237	56237	56237	56699					

[a] Relative to $3s^23p(^2P)$ total energy of $-241.934137E_H$.

[b] Percentage of normalized CI wave function.

[c] Denotes number of diffuse *d* functions added to [7*s* 6*p* 4*d* 3*f*] basis.

[d] Moore (1949), Wiese *et al.* (1969).

[e] Penkin and Shabanova (1963,1965), result in parentheses from Budick (1966).

[f] See text.